

Use of Factorial Design in the Study of the Influence of Firing Cycle Parameters on the Technological Properties of a Brazilian Kaolinitic Material

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Abstract

The firing cycle is an important variable in the production of red ceramics, which contributes to high energy demand. In this work the simultaneous effects of the firing cycle parameters (firing temperature and heating rate) on the technological properties of a kaolinitic material were evaluated by using the factorial design. The specimens were prepared by extrusion and fired at temperatures ranging from 700 to 1100 °C using different heating rates (1 °C/min, 10 °C/min, and 20 °C/min). The following technological properties were determined: linear shrinkage, apparent density, water absorption, and flexural strength. By using 3² factorial designs, it was found that the firing temperature is the main controlling factor of the technological properties of the kaolinitic material. The results obtained by factorial design also indicated that the kaolinitic material could support the use of rapid heating rate (up to 20 °C/min) in the production of red ceramics.

Keywords

Kaolinitic Material; Firing Cycle; Factorial Design

Introduction

The term red ceramic is used to designate the clay-based products with reddish colour [1]. The red ceramic industry is focused on the manufacturing of building materials such as bricks, ceramic blocks, roofing tiles, and tubes. In general, the common clays are the most widely used raw materials for red ceramics. Common clays are present in every country in the world. The mineral composition of these clays is quite variable, but usually illite, chlorite and kaolinite are the most common clay minerals present. The technological properties of red ceramics are influenced

by several factors such as: i) chemical, mineralogical and physical characteristics; and ii) processing operations such as shaping, drying, and firing [2]. In particular, the firing cycle parameters (temperature, time, and heating rate) have a marked influence on the technological properties [3]. Conventionally, red ceramics require a slow-firing cycle that can reach up to 60 h (cold to cold). As a result, the firing process of red ceramics requires high demand of energy. This situation is not desirable because of the serious economic and environmental constraints.

The fast-firing process has been successfully used in the production of several ceramic materials [3-13]. The main advantages of this process are: i) increased energy efficiency; ii) higher productivity (less time to firing); and lower environmental impact. Despite its importance, few studies have been conducted on the fast-firing process in the field of the red ceramic. In particular, there is need for most studies on the fast-firing cycles applied in different common clays used in the red ceramic industry worldwide.

The purpose of this study was to investigate the effects of firing cycle parameters (firing temperature and heating rate) on the technological properties of a Brazilian kaolinitic material used in red ceramics using factorial design. The factorial design approach has been used successfully in several fields [14-16], and is extremely useful for measuring the effects (or influence) one or more variables on the response of a process. It allows a combination of all variables at all levels, thus obtaining an analysis of a variable, subject to all the other combinations.

Material and Methods

Material

The kaolinitic material body used in the experimental study was collected from a red ceramic plant located in south-eastern Brazil (Campos's dos Goytacazes-RJ). The chemical composition of the kaolinitic material body is given in Table I. In addition, the clayey body consists mainly of kaolinite, and quartz, illite/mica, gibbsite, hematite, and microcline as accessory minerals. The texture analysis of the clayey body (clay, silt, and sand fractions: 31 %, 55 %, and 14 %) showed that it has high content of fine particles and high plasticity (37 %), which is mainly due to the presence of kaolinite.

TABLE 1 CHEMICAL COMPOSITION OF THE KAOLINITIC MATERIAL

Oxides	wt. %
SiO ₂	40.31
Al ₂ O ₃	32.15
Fe ₂ O ₃	10.83
TiO ₂	1.49
K ₂ O	2.32
Na ₂ O	0.62
CaO	0.32
MgO	0.78
MnO	0.10
Loss on ignition (1000 °C)	11.03

Processing and Testing

Test specimens in the form of rectangular bars (90 mm x 35 mm x 15 mm) were prepared by industrial extrusion, and then dried at 110 °C for 24 h. Firing step was carried out at peak temperatures of 700, 900 and 1100 °C for 1h using different heating rates (1 °C/min, 10 °C/min, and 20 °C/min). For comparison, the heating rate of 1 °C/min (conventional slow-firing rate) was used as reference.

The linear shrinkage of the fired specimens was measured according to the ASTM C326 standard. The apparent density was determined by the Archimedes method according to the ASTM C373 standard. The water absorption was determined from weight differences between the as-fired and water saturated pieces (immersed in boiling water for 2h) following the procedure reported in the ASTM C373 standard.

The flexural strength of the test specimens was determined with the three-point bending test, using a loading rate of 0.5 mm/min according to the ASTM C674 standard. Scanning electron microscopy operating at 15 kV was used to examine gold-coated fracture surfaces of the fired specimens via secondary electron images (SEI). The crystalline phase analysis after firing was done via X-ray diffraction with Cu-K α radiation.

Methodology of the Factorial Design

To evaluate the influence of the processing variables (firing temperature and heating rate) on the technological properties of the kaolinitic material was proposed a three-level factorial design 3². This design involves two factors (A and B), three levels, and n replicates. The mathematical model can be expressed as [15]:

$$y_{ijk} = \mu + \tau_i + \beta_j + (\tau\beta)_{ij} + \varepsilon_{ijk} \quad (1)$$

in which the parameter μ denotes the global mean, τ_i denotes the effect of the i th treatment of factor A, β_j denotes the effect of the j th treatment of factor B, $(\tau\beta)_{ij}$ denotes the effect of interaction between τ_i and β_j , and ε_{ijk} is the random error that follows the standard normal distribution. The treatment effects of the two factors are considered deviations from the global mean. Thus,

$$\sum_{i=1}^a \tau_i = 0 \quad (2)$$

and

$$\sum_{j=1}^b \beta_j = 0 \quad (3)$$

Furthermore, the interaction effects are defined such that

$$\sum_{i=1}^a (\tau\beta)_{ij} = \sum_{j=1}^b (\tau\beta)_{ij} = 0. \quad (4)$$

The experimental points of the 3² factorial design used in this work are illustrated in Fig. 1, and their combinations are summarized in Table II. The demonstration of the efficiency of the generated model was performed using analysis of variance (ANOVA) [14]. According to the mathematical expressions, the response surfaces for each ceramic property against the firing cycle parameters (firing temperature and heating rate) was carried out with the software Statistica.

TABLE 2 EXPERIMENTAL POINTS OF THE FIRING CYCLE PARAMETERS

Experimental point	Heating Rate (°C/min)	Firing Temperature (°C)
1	1	700
2	1	900
3	1	1100
4	10	1100
5	20	1100
6	20	900
7	20	700
8	10	700
9	10	900

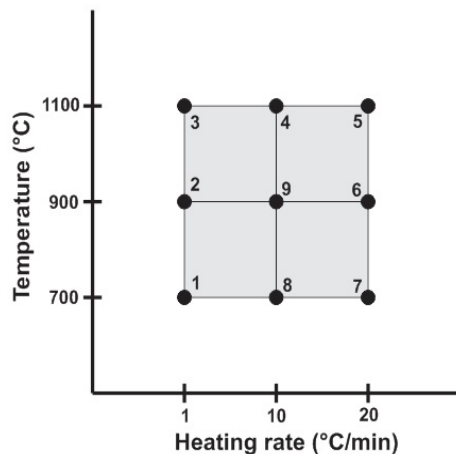


FIG. 1 EXPERIMENTAL POINTS USED IN THE FACTORIAL DESIGN APPROACH

Results and Discussion

The measured values of the technological properties (Linear Shrinkage – LS, Apparent Density – AD, Water Absorption – WA, and Flexural Strength – FS) of the fired test specimens as a function of the firing cycle parameters (firing temperature and heating rate) are given in Table III. A regression equation was obtained for each ceramic property using factorial design, at a 5 % level of significance. All regressions had high coefficient of determination ($R^2 = 0.9208 - 0.1000$). This means that the regression models obtained have low variability, and are to be considered statistically significant.

TABLE 3 TECNOLOGICAL PROPERTIES OF THE FIRED TEST SPECIMENS: LS – LINEAR SHRINKAGE, AD – APPARENT DENSITY, WA – WATER ABSORPTION, AND FS – FLEXURAL STRENGTH

Property	1 °C/min		
	700 °C	900 °C	1100 °C
LS, %	0.62	1.75	9.65
AD, g/cm ³	1.45	1.66	2.05
WA, %	30.10	26.15	9.79
FS, MPa	3.69	5.24	12.96
Property	10 °C/min		
	700 °C	900 °C	1100 °C
LS, %	0.98	1.91	9.39
AD, g/cm ³	1.45	1.58	2.05
WA, %	35.00	27.06	10.10
FS, MPa	4.84	5.16	10.06
Property	20 °C/min		
	700 °C	900 °C	1100 °C
LS, %	1.19	1.24	9.14
AD, g/cm ³	1.45	1.58	2.06
WA, %	34.09	27.42	11.77
FS, MPa	4.36	5.06	9.02

Fig. 2 shows the Pareto diagram for each technological property. This diagram demonstrates the effects that are statistically significant. Thus, the evolution of the technological properties against the firing cycle parameters according with the methodology of factorial design, obey the following equations:

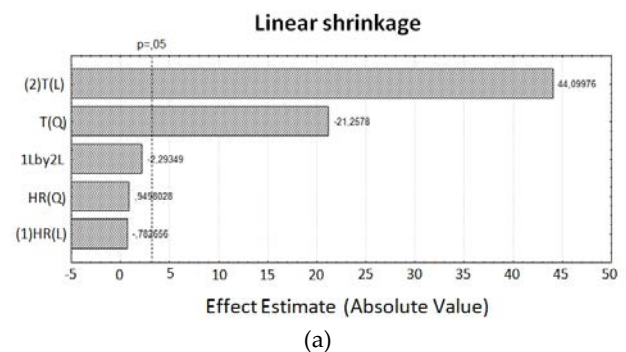
$$LS(\%) = 54.0396 - 0.1375T + 0.0001T^2 \quad (5)$$

$$AD(g/cm^3) = 3.1854 - 0.0050T + 0.00001T^2 \quad (6)$$

$$WA(\%) = 25.1096 + 0.1718T - 0.0001T^2 \quad (7)$$

$$FS(MPa) = 8.1275 + 0.0166T \quad (8)$$

in which T is the firing temperature.



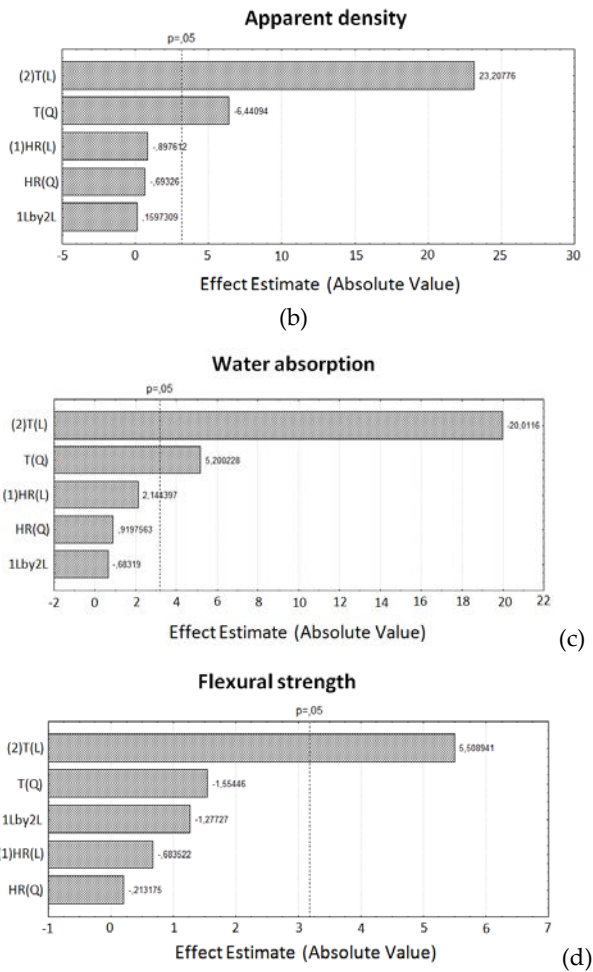


FIG. 2 PARETO DIAGRAM FOR EACH TECHNOLOGICAL PROPERTY MEASURED: A) LINEAR SHRINKAGE; B) APPARENT DENSITY; C) WATER ABSORPTION; AND D) FLEXURAL STRENGTH

Fig. 3 shows the statistical behavior of the technological properties in terms of prescribed values versus observed values. It can be seen a linear relationship to correlate the predicted and observed values for all the studied properties. This means that the 3^2 factorial design can be adopted for modeling the effects of the firing cycle parameters on the technological properties of the kaolinitic material to a very high degree of confidence.

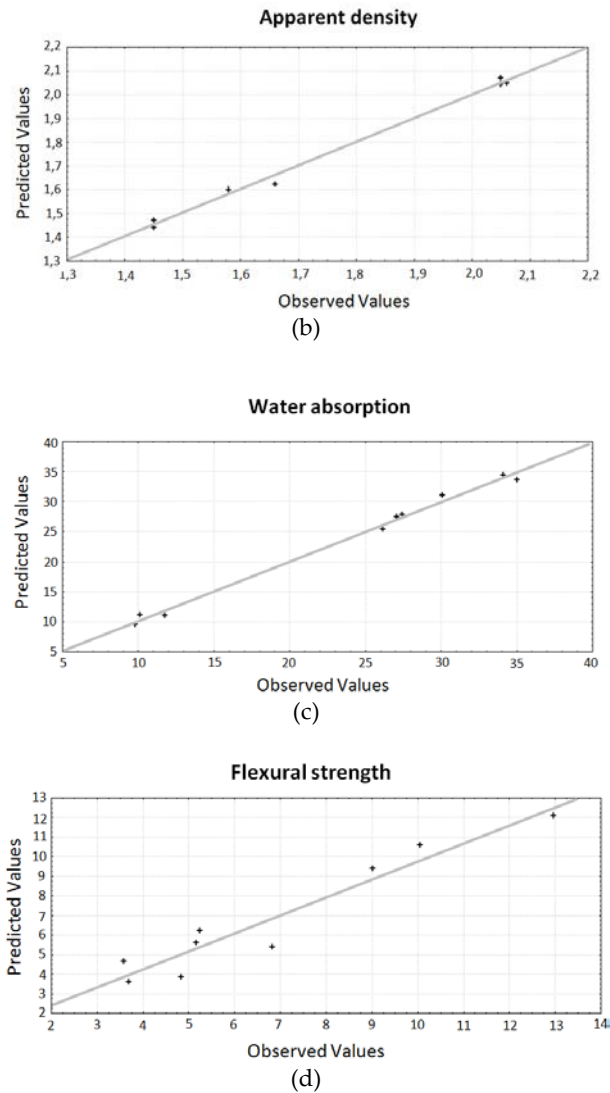
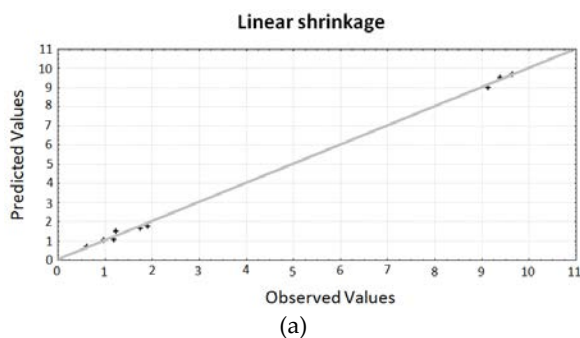


FIG. 3 STATISTICAL BEHAVIOR FOR EACH TECHNOLOGICAL PROPERTY: OBSERVED VALUES VERSUS PRESCRIBED VALUES. A) LINEAR SHRINKAGE; B) APPARENT DENSITY; C) WATER ABSORPTION; AND D) FLEXURAL STRENGTH

Fig. 4 shows the calculated response surfaces for each technological property (LS, AD, WA, and FS) of the fired test specimens. These 3D surfaces correspond to graphical representation of equations (5) to (8), and are very helpful in determining the response value for the firing parameters investigated. The responses surfaces allowed the simultaneous assessment of both variables (firing temperature and heating rate), and also the determination of the regions with best performances of the technological properties. It can be seen that the higher firing temperature, the better technological properties (lower water absorption and higher mechanical strength) are obtained. However, the heating rate had little influence on the technological properties.

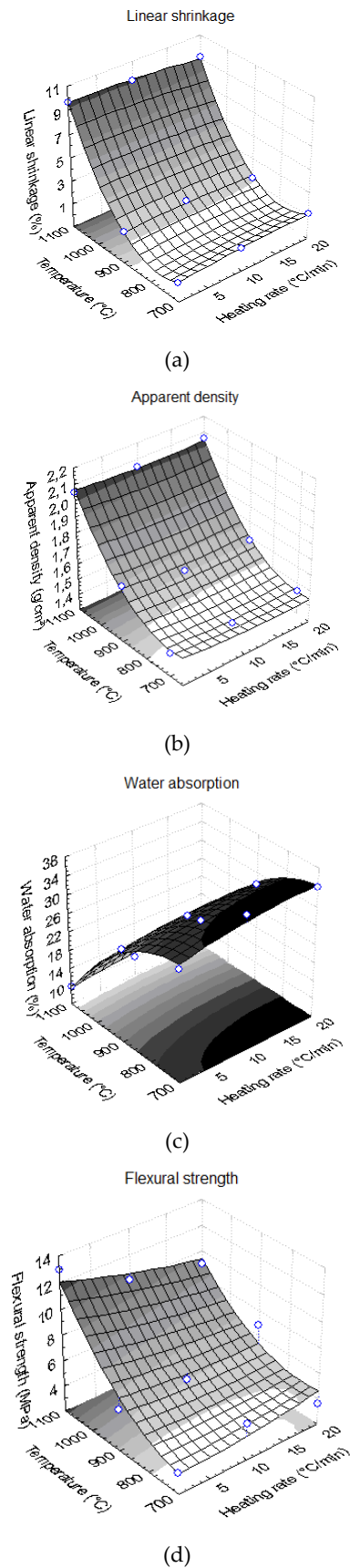


FIG. 4 RESPONSES SURFACE PLOTS FOR EACH TECHNOLOGICAL PROPERTY: A) LINEAR SHRINKAGE; B) APPARENT DENSITY; C) WATER ABSORPTION; AND D) FLEXURAL STRENGTH

The evolution of the technological properties as a function of the firing cycle parameters is shown in Fig. 5a-d. The correlation between the evolution of the technological properties and the low degree polynomials described in eqs. (5) to (8) is well established.

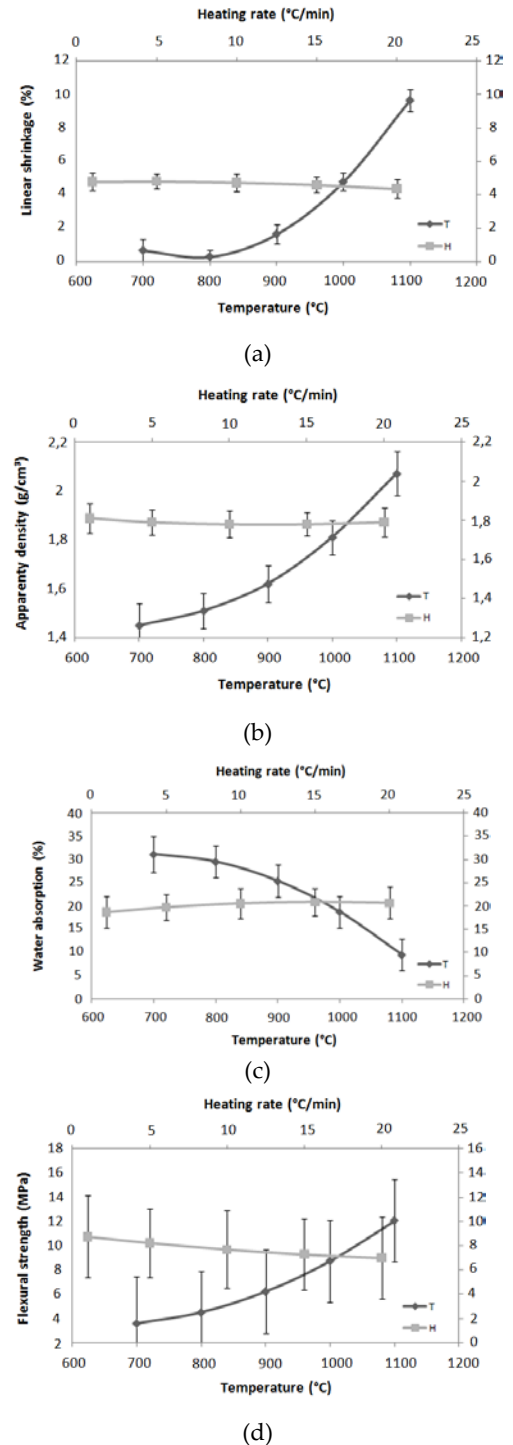


FIG. 5 EVOLUTION OF THE TECHNOLOGICAL PROPERTIES AS A FUNCTION OF FIRING CYCLE PARAMETERS: A) LINEAR SHRINKAGE; B) APPARENT DENSITY; C) WATER ABSORPTION; AND D) FLEXURAL STRENGTH

An analysis of Fig. 5a indicates that the firing temperature is the main controlling parameter of the linear shrinkage of the specimens. This behavior can be attributed to major sinterability of the specimens. However, the linear shrinkage behaves differently below and above 800 °C. The specimens showed low firing shrinkage up to 800 °C, in which the sintering was dominated by particle-to-particle contact mainly of metakaolinite platelets. In this temperature range solid state sintering mechanism is dominant [17]. Above of 800 °C, however, the specimens presented higher values of linear shrinkage. In this case, the specimens sintered prevalently by viscous flow. The higher the firing temperature the lower the viscosity, and larger the volume of the glassy phase formed. Fig. 5a also shows that no significant differences can be recognized in the linear shrinkage of the specimens fired under different heating rates. This means that the heating rate has little influence on the degree of densification of the kaolinitic material pieces. This finding is in accordance with the apparent density values (Fig. 5b).

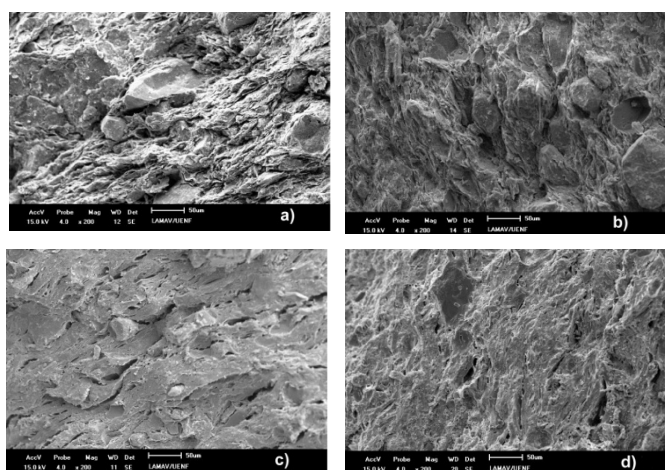


FIG. 6 SEM IMAGES OF THE SPECIMENS AT DIFFERENT TEMPERATURES AND HEATING RATES: A) 700 °C AT 1 °C/MIN; B) 900 °C/MIN; C) 1100 °C/MIN; AND D) 1100 °C/MIN AT 20 °C/MIN

The evolution of water absorption, as shown in Fig. 5c, is strongly influenced by firing temperature mainly above 800 °C. The water absorption decreases with the increase of the firing temperature. The glassy phase by the capillarity action and surface tension infiltrates the open pores of the structure and causes densification of the kaolinitic material pieces. Fig. 5c also showed that the heating rate did not influence the water absorption of the specimens. It is well known that the water absorption is related to the microstructure of the sintered ceramic matrix, and determines the level of open porosity of the fired

specimens. Fig. 6a-d shows the evolution of the microstructure of the specimens as firing temperature increases. The effect of the firing temperature was to increase the densification with progressive pore closure (Fig. 6a-c). However, the slow-fired piece (Fig. 6c) had a microstructure very similar to that of fast-fired piece (Fig. 6d). This means that rapid heating rate does not cause significant variation on the texture and porosity of the kaolinitic material pieces. These results are in accordance with the values of linear shrinkage (Fig. 5a) and apparent density (Fig. 5b). XRD patterns of the specimens fired at 900 °C under different heating rates are presented in Fig. 7. The resulted indicated the presence of the following crystalline phases for both heating rates: illite/mica, quartz, microcline, and hematite. It is noticed that only small differences in the peak intensities occurred. For both XRD patterns the peaks of kaolinite are not seen. Kaolinite is transformed into amorphous metakaolinite. Thus, the use of higher heating rate also didn't change the crystalline phases present in the fired specimens.

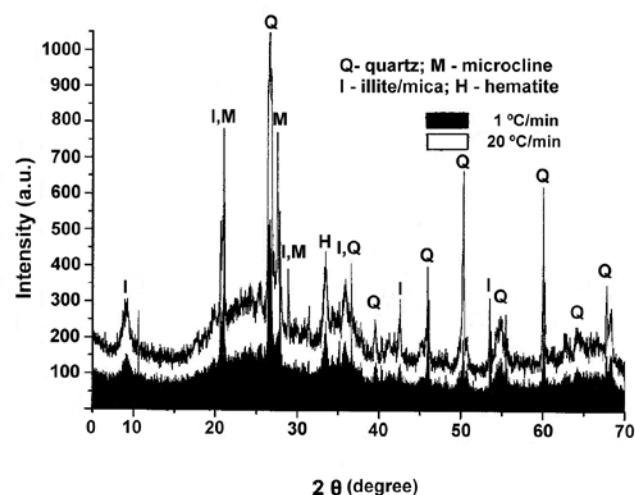


FIG. 7 X-RAY DIFFRACTION PATTERNS OF THE SPECIMENS FIRED AT 900 °C UNDER DIFFERENT HEATING RATES

The variation of the flexural strength as a function of the firing cycle parameters is given in Fig. 5d. The mechanical behavior is quite correlated to all other studied properties. These results are well visualized by the response surfaces (Fig. 4). The firing temperature is the main controlling factor of the flexural strength. This behavior is in agreement with the concomitant increases of the densification (Fig. 5b). It is known that the porosity influence negatively mechanical strength. Thus, the pore closure must cause an increase of the flexural strength. This is particularly observed above 800 °C, as the densification rate is high. On the other hand, the

flexural strength was not changed with increasing heating rate. This means that rapid heating rate (fast-firing) seems to be adequate for the production of red ceramics using kaolinitic material.

The use of the 3^2 factorial design approach showed that the firing temperature and heating rate interacts in a different way on the technological properties of kaolinitic material. It was also shown that the firing temperature is the firing cycle parameter more important. The higher the firing temperature is, the lower the open porosity of the kaolinitic material pieces are. As a result, higher quality red ceramics can be obtained. The effects of the heating rate on the technological properties have been less pronounced. In fact, the values of technological properties of the kaolinitic material pieces obtained by using a slow-firing cycle (1 °C/min) showed only small differences to those obtained by using a fast-firing cycle (20 °C/min). These results are well visualized by the response surfaces (Fig. 4). The duration of the total firing-cooling cycle at 1 °C/min is between 24 to 38 h, depending on the firing temperature, while the 20 °C/min is 2.2 to 2.8 h. These results are very important because the use of rapid heating rate (i.e., fast-firing cycle) seems to be adequate for processing of red ceramics using kaolinitic material, without sacrificing the technological properties. In addition, the use of rapid heating rate can provide significant economic and environmental benefits because of the possibility of using a shorter firing cycle.

Conclusions

The results of this investigation indicated that the 3^2 factorial design approaches is an effective tool to evaluate the effects of the firing cycle parameters (firing temperature and heating rate) on the technological properties of a kaolinitic material used in red ceramics. The calculated regression models for each technological property were found to be statically significant and presented low variability. The kaolinitic material used can support the use of fast-firing cycle (up to 20 °C/min) without major sacrifices of the technological properties (linear shrinkage, apparent density, water absorption, and flexural strength). This investigation has also demonstrated that the firing temperature is the main controlling factor of the technological properties. Aside from the economical and environmental benefits of reducing the total duration of the firing cycle, the use of rapid heating rate allows the production of red ceramics

using kaolinitic material with good technical properties.

ACKNOWLEDGMENT

The authors acknowledge the CNPq and FAPERJ for supporting this work.

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